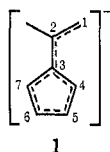


Protonation of the Isopropenylcyclopentadienyl Anion^{1a}JACK HINE^{1b} AND DAVID B. KNIGHT^{1c}*Departments of Chemistry, The Ohio State University, Columbus, Ohio 43210, and The University of North Carolina at Greensboro, Greensboro, North Carolina 27412*

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The reaction of isopropenylcyclopentadienylpotassium with aqueous acid gives a mixture containing, in order of decreasing yield, the linearly conjugated product 1-isopropenyl-1,3-cyclopentadiene (4), the cross-conjugated product 2-isopropenyl-1,3-cyclopentadiene (5), and 6,6-dimethylfulvene (2) under conditions where the smallest amount of subsequent isomerization of initially formed products is believed to have occurred. The equilibrium mixture of these isomers at room temperature contains about 98% 2, 1.4% 4, and 0.6% 5. It is possible that the deconjugated product 5-isopropenyl-1,3-cyclopentadiene (3), believed to be the least stable of the four possible isomers, was also formed in significant amounts in the protonation reaction but that it rearranged before the product mixture was analyzed.

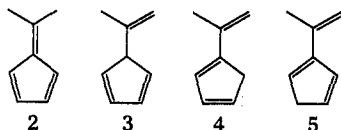
In an earlier paper² certain data on the protonation of resonance-stabilized carbanions were rationalized in terms of the principle of least motion.³ In this connection the protonation of the isopropenylcyclopentadienyl anion (1) is of interest. Protonation at carbon 1 gives



the most stable product. Protonation at carbon 3 would be accompanied by the smallest changes in bond lengths and essentially the same changes in bond angles as in the other cases. According to an HMO calculation, carbons 4 and 7 have the greatest electron density; hence their protonation might be expected to be accompanied by the least change in electronic configuration.

Results

Simple protonation of carbanion 1 can give dimethylfulvene (2), the deconjugated product 5-isopropenyl-1,3-cyclopentadiene (3), the linearly conjugated product 1-isopropenyl-1,3-cyclopentadiene (4), or the cross-conjugated product 2-isopropenyl-1,3-cyclopentadiene (5). Treatment of a heterogeneous slurry of potassium



tert-butoxide in bis(2-methoxyethyl) ether (diglyme) with 1 equiv of dimethylfulvene (containing a small amount of dicyclopentadiene as a reference compound) gave a homogeneous brown-red solution presumed to contain carbanion 1. This solution was added to aqueous acid in the presence of a separate layer of organic solvent at various temperatures. The resultant yellow organic layer was washed and analyzed by gas-liquid partition chromatography (glpc), sometimes before and sometimes after the solvent was removed to give an amber liquid whose properties changed significantly if

it was allowed to remain at room temperature for as long as 30 min. The glpc analysis usually showed only peaks for dicyclopentadiene, dimethylfulvene, and a third component with a somewhat shorter retention time, which is believed to be due to isomers of dimethylfulvene. In some cases the dicyclopentadiene content of these products was essentially the same as that of the reactant, showing that probably no significant amounts of other products were formed. The area of the isomer peak ranged from somewhat less than that of the dimethylfulvene peak to 7.5 times as large. There was no clear difference between the results obtained using the different protonation procedures.

The isomer peak was separated from the amber liquid by preparative glpc. Its mass spectrum was identical with that of dimethylfulvene at 70 eV but not at 12.5 eV. These observations, including the parent peak at mass 106, give strong evidence that one or more of the isomers 3, 4, and 5 were present. This interpretation is supported by the infrared spectrum, which contained a strong peak at 895 cm⁻¹ and a weak peak at 1780 cm⁻¹, characteristic of -C=CH₂ groups.⁵

The 100-MHz proton magnetic resonance spectrum of the "isomer mixture" showed absorption in four regions, τ 3.20-3.80, 4.75-5.30, 6.85-7.05, and 7.95-8.10 ppm, with relative areas of 3.1:2.07:2.07:3.00, which were assigned to hydrogen atoms attached to unsaturated ring carbon atoms, exocyclic vinyl hydrogen atoms, ring methylene hydrogen atoms, and methyl hydrogen atoms, respectively. The assignments are supported by analogy to the unsaturated ring hydrogen atoms of the methylcyclopentadienes⁶ (τ 3.6-4.0 ppm), the terminal unsaturated hydrogen atoms of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene⁷ (τ 4.8-5.0 ppm), the ring methylene hydrogen atoms of 1- and 2-methylcyclopentadiene⁶ (τ \sim 7.2 ppm), and the methyl groups of 2,3-dimethyl-1,3-butadiene⁷ (τ \sim 8.0 ppm), respectively. The relative areas of the four regions of absorption are as expected for compounds 4 and 5 but not for 3. Since the methinyl hydrogen atoms of 5-methylcyclopentadiene absorb at τ 6.97 ppm and replacing the methyl by a vinyl group would be expected to shift the absorption 0.5-1.0 ppm lower, compound 3 should absorb in the range 6.0-6.5 ppm. No absorption in this range was observed. For these reasons and the fact that we can explain essentially the entire spectrum

(1) (a) This investigation was supported in part by Grant GP-4445 from the National Science Foundation. (b) The Ohio State University. (c) The University of North Carolina at Greensboro.

(2) J. Hine, *J. Org. Chem.*, **31**, 1236 (1966).

(3) "Those elementary reactions will be favored that involve the least change in atomic position and electronic configuration."⁴

(4) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938).

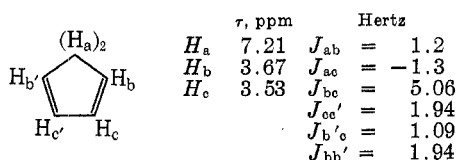
(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, pp 26, 50.

(6) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2313 (1965).

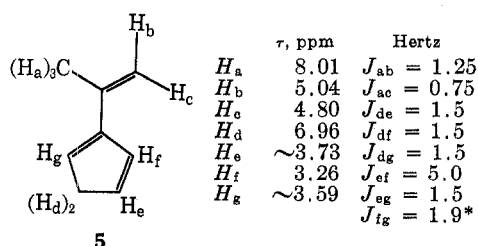
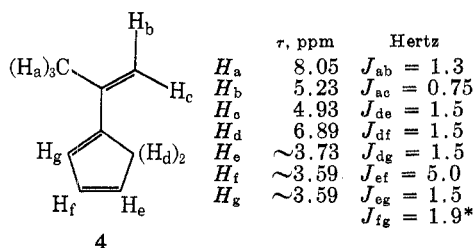
(7) R. Hobgood and J. H. Goldstein, *J. Mol. Spectrosc.*, **12**, 76 (1964).

without it, we believe that no appreciable amount of **3** is in the separated isomer mixture. The methyl region consisted of two slightly overlapping multiplets at τ 8.05 and 8.01 ppm with relative areas of about 68:32. The methylene region consisted of a doublet of doublets at τ 6.89 and a broad peak at 6.96 ppm, with relative areas of about 71:29. The exocyclic vinyl hydrogen region contained a pair of larger and a pair of smaller broad peaks with relative areas about 73:27. Decoupling experiments showed that the larger peaks in one region were in the same molecule as the larger peaks in another region. These observations suggest that the material is a mixture containing about 70% of one component and 30% of another. The composition of this mixture remained relatively constant from run to run even though the amount of dimethylfulvene formed varied considerably.

The unsaturated ring hydrogen region contained, with relative areas of about 1:1.64:0.22, a multiplet at τ 3.73, a multiplet at 3.59, and, at 3.26 ppm, a doublet ($J = 5$ Hz) of quartets ($J = 1.5$ Hz) that became a doublet ($J = 5$ Hz) of doublets ($J = 1.5$ Hz) upon irradiation at τ 6.96 ppm. These observations require that the unsaturated ring hydrogen atoms of the less abundant component absorb at τ 3.26, about 3.59, and about 3.73 ppm, and that those of the more abundant component absorb at about 3.59, 3.59, and 3.73 ppm. From the following analysis of the pmr spectrum of cyclopentadiene by Manatt⁸ and similar data, we concluded that the hydrogen atoms at the ends of π sys-



tems in our compounds absorbed at higher field than those attached to the interior carbon atoms. These considerations and additional apparent coupling constants, largely from decoupled spectra, led to the following assignments for the pmr spectra of **4** and **5**. The



peaks at τ 3.59 and 3.73 ppm were never clearly separated and therefore the chemical shifts so listed are more uncertain than the others. The starred coupling con-

stant (J_{ig}) was not derived from any of our measurements but was assumed by analogy to cyclopentadiene. The coupling constants listed are all plausible (the best models for the last six being those in cyclopentadiene), but they would also be if the assignments for the two compounds were reversed. Hence, the two compounds were distinguished on the basis of chemical shifts.

The carbon skeletons of compounds **4** and **5** would be expected to be nearly coplanar in order to maximize overlap between the π systems of the rings and those of the isopropenyl groups. Therefore the ring protons will be deshielded by the isopropenyl group, and the methylene protons in **4** will be more deshielded than the more distant methylene protons in **5**.⁹ Conversely, the protons of the isopropenyl group will be more deshielded by the double bond to which H_e and H_f are attached in **5** than in **4**. Thus the major component of the mixture, whose methylene protons absorb at lower field and whose isopropenyl protons absorb at higher field than those of the minor component, must be **4**. The fact that the methylene protons are not in the plane of the carbon skeleton probably makes the difference in chemical shifts for these protons smaller than it would otherwise be. This is partly true for the methyl protons, but the fact that these protons in **4** and **5** have so nearly the same chemical shift also suggests that the isopropenyl group is oriented as shown in the formulas, with its double bond trans to the ring double bond with which it is conjugated.

As the product mixture stood, new pmr peaks appeared and grew at the expense of those due to **2**, **4**, and **5**. The fraction of the absorption appearing above τ 6.0 ppm increased from about 54% initially to 63% after 4 hr at 37°, when at least 58% of the **4** and about 38% of the **5** had disappeared. After 280 hr, when all the **4** and **5** and about half the dimethylfulvene were gone, 68% of the absorption was above τ 6.0 ppm.

In order to learn more about the relative stabilities of compounds **2-5**, samples of dimethylfulvene were treated with small amounts of base in 85:15 diglyme-*tert*-butyl alcohol and in *tert*-butyl alcohol. Equilibrium seemed to have been reached when about 98.8% dimethylfulvene and 1.2% of material with the retention time of **4** and **5** were present. Equilibrium was approached from the other side by use of a mixture containing about 40% dimethylfulvene and 60% **4** and **5**, which was treated in the same way. Equilibrium seemed to be near when 96.5% dimethylfulvene and 3.5% of material with the retention time of **4** and **5** were present, but slow side reactions made it impossible to wait indefinitely for the establishment of equilibrium. A small amount of the minor component of the equilibrium mixture obtained starting with dimethylfulvene was separated by glpc and found to have an ultraviolet spectrum (maxima at 212 and 288 $m\mu$ with shoulders at 214 and 216 $m\mu$) almost identical with that of the major glpc fraction from the protonation of carbanion **1** and quite different from that of dimethylfulvene (maxima at 266, 271, and 354 $m\mu$). Taking the position of equilibrium as intermediate between that attained starting from the two different sides, we estimate

(9) Somewhat similar effects may be seen in the pmr spectra of 6-phenylfulvene¹⁰ and 6-vinylfulvene.¹¹

(10) M. L. Heffernan and A. J. Jones, *Aust. J. Chem.*, **19**, 1813 (1966).

(11) J. M. Neuenschwander, D. Meuche, and H. Schaltegger, *Helv. Chim. Acta*, **47**, 1022 (1964).

(8) S. L. Manatt, Jet Propulsion Laboratory, California Institute of Technology, personal communication, 1967.

that the equilibrium mixture of isomers contains about 98% dimethylfulvene, 1.4% **4**, 0.6% **5**, and too little **3** to detect.

In view of the possibility that some isomerization may have occurred during the glpc separation (at 115°), the products of protonation of **1** were not separated in several runs. In one run in which the product mixture had been distilled (at room temperature and reduced pressure), the ultraviolet spectrum was found to contain all the absorbance peaks characteristic of dimethylfulvene and the mixture of **4** and **5**, separated by glpc, except that the 288 m μ peak became a shifted shoulder on the stronger dimethylfulvene peak at 271 m μ . In addition, there was an unexplained peak at 253 m μ . The pmr spectrum of material that had been extracted but not distilled showed all the peaks found in the two fractions obtained when glpc separation was used. Integration of these peaks showed that about 20% dimethylfulvene, 55% **4**, 20% **5**, and 5% of the material that forms on standing was present.

When deuterium acetate in deuterium oxide was used as the quenching solution, the reaction product was found by mass spectral measurements to be about 66% monodeuterated and 12% dideuterated. The combined yield of **4** and **5** in this run was 4.4 times that of dimethylfulvene.

Discussion

We may use dimethylfulvene as a standard and define the stabilities of the isomers in terms of $\Delta G^\circ_{\text{chem}}$ ¹² for their formation from dimethylfulvene. From our equilibrium measurements and the symmetry numbers of dimethylfulvene (18), **4** (3), and **5** (3), values of 0, 3.6, and 4.1 kcal/mol may be calculated for the respective $\Delta G^\circ_{\text{chem}}$ values at room temperature. Simple HMO calculations give the same delocalization energies for **2**, **3**, **4**, and **5** as for fulvene (1.466 β), 1,3-butadiene (0.472 β), 1,3,5-hexatriene (0.988 β), and 3-methylene-1,4-pentadiene (0.899 β), respectively.^{13a} A plot of the three known values of $\Delta G^\circ_{\text{chem}}$ vs. the corresponding delocalization energies gives a surprisingly good straight line of slope -7.2 kcal/ β , in satisfactory agreement with -6 kcal/ β , the average value for polyenes.^{13b} This correlation supports the structural assignments **4** and **5** made for the more and less stable components of the isomer mixture. Extrapolation of the plot gives a $\Delta G^\circ_{\text{chem}}$ value of 7.3 kcal/mol for **3**, from which **3** may be estimated to comprise less than 0.001% of the equilibrium mixture of isomers.

The starting dimethylfulvene not accounted for in our glpc analyses may have been lost partly because of its significant volatility and solubility in aqueous diglyme. However, reactions to give products of higher molecular weight, perhaps *via* Diels-Alder reactions, probably also contributed. The variation in yields of dimethylfulvene may be due to isomerization of the kinetically controlled product mixture by a carbanion mechanism, perhaps partly because of local excesses of base present during the protonation reaction. Since there would certainly be no significant net rearrangement of dimethylfulvene to the other isomers, the fraction of dimethylfulvene present in the original kinet-

ically controlled product mixture should be as low as, or lower than, that obtained in any run (since dimethylfulvene gives higher molecular weight products more slowly than do **4** and **5**). The presence of dideuterated products in the reaction mixture obtained using deuterium acetate shows that some carbanion formation by **4** and **5**, and hence some isomerization to dimethylfulvene, have occurred (in a run in which about 18% dimethylfulvene was formed).¹⁴ Thus, it is not clear that protonation of carbanion **1** to give the most stable of the possible products occurs to a greater than random extent (16 2/3%), and it may occur to a considerably smaller extent.

Further interpretation of our results is limited by our ignorance of whether **3** is formed or not. If **3** were formed from **1** and then rearranged *via* reversion to **1** (perhaps during the work-up), the relative yields of the other three isomers would not be affected. However, the isomerization of **3** by a sigmatropic migration of hydrogen should give **4** specifically. The fact that the ratio of **4** to **5** appears to move away from the equilibrium ratio as the compounds are transformed to higher molecular weight products on standing at 37° suggests that **4** and **5** are not interconverted very rapidly. It therefore appears that the **4** observed may be the sum of that formed directly by protonation of **1** and that formed indirectly *via* rearrangement of **3**.

We believe that the following facts are relevant to consideration of the relative rates of protonation of the various carbon atoms of carbanion **1**. A simple estimate of the magnitude of the least nuclear motion effect, the sums of the squares of the changes in bond numbers that accompany the reactions,² gives the values 0.89, 1.22, 1.55, and 2.22 for the formation of **3**, **5**, **4**, and **2**. A semiquantitative method of estimating the least nuclear motion effect from force constants and changes in bond length² gives the same sequence, except that the values for **4** and **5** are close to each other and become essentially equal when certain methods of estimating molecular geometry are used. An HMO calculation gives charge densities of -0.187 , -0.182 , -0.162 , and -0.116 at the carbon atoms whose protonation gives **4**, **5**, **3**, and **2**, respectively, but calculation by an SCF MO method¹⁵ gives the greatest negative charge density at the carbon atom whose protonation gives **2**.¹⁶ More detailed application of these least nuclear motion effects and charge densities to the problem of the protonation of **1** is probably not warranted until a larger fraction of the dimethylfulvene used can be unambiguously accounted for, subsequent isomerization of initially formed products can be consistently minimized, and it can be learned whether **3** is formed or not.

(14) The oxygen-bound hydrogen atoms in the deuterium acetate quenching mixture contained about 6% protium, largely from the *tert*-butyl alcohol formed in the generation of carbanion **1**. The observed formation of about 22% undeuterated products might be due to a kinetic isotope effect, but much of the product may have been formed before the local excesses of protium that initially surrounded the carbanions had been dispersed by mixing. It seems unlikely that the reaction of the carbanion was complicated by the presence of a two-phase system. Diglyme and water are completely miscible and a second phase does not appear when the reaction mixture is poured into an aqueous solution until after the isomer mixture has been formed and its molecules had a chance to agglomerate. When the quenching experiments were carried out in the presence of a lower layer of carbon tetrachloride, the reaction was probably essentially complete before contact with the carbon tetrachloride.

(15) O. W. Adams and R. L. Miller, *Theor. Chim. Acta*, **12**, 151 (1968).

(16) R. L. Miller, University of North Carolina at Greensboro, personal communication, 1969.

(12) S. W. Benson, *J. Amer. Chem. Soc.*, **80**, 5151 (1958).

(13) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, (a) pp 43, 44, 95, or calculated by the methods given; (b) p 242.

Experimental Section¹⁷

Dimethylfulvene.—The method of Freiesleben¹⁸ was used to obtain dimethylfulvene (5-isopropylidene-1,3-cyclopentadiene), which was found to contain about 10% dicyclopentadiene. Fractional freezing was used to reduce the dicyclopentadiene content to about 5%, at which level it was used as a reference in glpc analysis of the reaction products. Pure dimethylfulvene was obtained by preparative glpc: mass spectrum (12.5 eV) *m/e* (rel intensity) 107 (9.0), 106 (100), 105 (0.6), 91 (4.6), 66 (1.2).

Reaction of 1-Isopropenyl-2,4-cyclopentadienylpotassium with Acid.—In a typical run a slurry of 11.0 g (98 mmol) of potassium *tert*-butoxide in 20 ml of diglyme (distilled over sodium and stored over Molecular Sieves) was prepared under nitrogen in the 500-ml flask of a flame-dried glass system. A solution of 10.4 g (94 mmol of the principal component) of dimethylfulvene containing 4.4% dicyclopentadiene in 5 ml of diglyme was added with stirring to the slurry, which had been cooled to 3°. The resulting red-brown solution was homogeneous at 20° but cloudy at 5°, at which temperature it was added rapidly to a separatory funnel containing 10 g of glacial acetic acid, 700 ml of water, and 200 ml of light petroleum ether, all at about 0°. After vigorous shaking a yellow-orange organic layer was present, which was washed twice with 700 ml of ice-cold water. The solvent was removed from the organic layer at reduced pressure and a temperature below 0° to give an amber liquid. Analysis *via* glpc on a 6-ft Apiezon L column at 100° showed 77.6% of the isomer-mixture peak at 8.0 min, 16.9% of dimethylfulvene at 11.75 min, and 5.3% of dicyclopentadiene at 21.5 min. The increase in dicyclopentadiene content shows that about 17% or more of the starting dimethylfulvene is unaccounted for, probably largely because of loss during removal of the solvent. In some runs in which the organic extract was analyzed without removing the solvent the dicyclopentadiene content was within the experimental uncertainty (~10%) of its original value. In other runs there was up to twice as much dicyclopentadiene in the products as in the reactant. In some of these cases the reaction mixtures had spent 1 hr or more at room temperature before analysis and in others the quenching solution had contained methanol (as an antifreeze agent), which may have retained more of the products, but in some cases the loss of product is not understood.

Reaction temperatures ranging from those obtained by Dry Ice cooling to room temperature were used, both hydrochloric and acetic acids were used, and diethyl ether and carbon tetrachloride were used instead of petroleum ether. Since the variation in yield of isomer mixture with reaction temperature seemed to be no larger than the variations observed at a given temperature, most of the later runs were carried out at room temperature using acetic acid rather than hydrochloric acid, which gave a smaller yield of isomers in the few cases in which it was used. The products obtained were stored at 0° or below. In several runs in which no significant loss of dimethylfulvene occurred, glpc analysis of the unconcentrated extracts showed a ratio of isomer mixture to dimethylfulvene of greater than 5:1, but in none of these cases was it possible to run 100-MHz pmr spectra on the products within a reasonable time after they were formed.

Sodium hydride and metallic sodium as the reagents and diethyl ether, dimethyl sulfoxide, and tetrahydrofuran as the solvents

for preparing a salt of dimethylfulvene usually gave darker colored reaction mixtures that reacted with acid to give little of the isomers of dimethylfulvene (and often little dimethylfulvene). Poor yields of the isomers were also usually obtained in quenching the carbanion with acetic acid in nonaqueous solvents.

The amber liquid product was separated by preparative glpc into dimethylfulvene and the light yellow isomer mixture: uv max (hexane) 211 m μ (ϵ 6490), 288 (6760); ir (neat) (in order of decreasing intensity) 895, 665, 1360, 2975, 2950, 2930, 880, 3090, 860, 2900, 1615, 1440, 1435, 1255, 2875, 955, 680, 705, 3050, 815, 1575, 780, 765, 925, 985, 1015, 625, 1230, 595, 575, 1315, 1000, 1105, 1280, 1125, 1090, 1780, and 2745 cm⁻¹; mass spectrum (12.5 eV) *m/e* (rel intensity) 107 (8.6), 106 (100), 105 (1.8), 92 (1.3), 91 (16), 80 (0.4), 78 (0.4), 66 (0.6).

Reaction of 1-Isopropenyl-2,4-cyclohexadienylpotassium with Deuterium Acetate.—In the deuteration experiment, the solution of 1 from 12.7 g (113 mmol) of potassium *tert*-butoxide and 11.9 g (108 mmol) of 95% dimethylfulvene-5% dicyclopentadiene in 35 ml of diglyme was divided into three equal portions. One was added to 5 g of acetic acid-*d*₄, 15 ml of 99.8% deuterium oxide, and 30 ml of carbon tetrachloride and then worked up in the usual way, with product being vacuum distilled. A second portion was quenched and worked up in the usual way using carbon tetrachloride and "light" water and acetic acid. Both products were analyzed by mass spectrometry at 9.0 eV where the only observed peaks for the protium product were at *m/e* 107, 106, and 66. The *m/e* 107 peak was 9.2% as large as the 106 peak, in good agreement with the value 8.8% calculated from 1.1% natural abundance of ¹³C. The assumption that every parent peak was accompanied by a parent + 1 peak 9.2% as large led to the values 22, 66, and 12% for the amounts of C₈H₁₀, C₈H₉D, and C₈H₈D₂ in the product formed using deuterium acetate.

Equilibration of Dimethylfulvene and Its Isomers.—When pure dimethylfulvene was heated to 100° for 23 hr, an intractable black sludge was formed. The same treatment in the presence of 5 mol % diphenylamine led to the recovery of 35% of the dimethylfulvene, but no isomers were detected. Solutions of dimethylfulvene in about 85% diglyme-15% *tert*-butyl alcohol containing less than 1 mol % potassium *tert*-butoxide were added to water-petroleum ether after various lengths of time at room temperature and the organic layer analyzed by glpc. After the content of isomer mixture reached 1-1.5%, the composition of the mixture no longer changed significantly. More isomer mixture was obtained from refluxing solutions and perhaps when stronger solutions of potassium *tert*-butoxide were used, but about the same results were obtained using triethylamine in *tert*-butyl alcohol. When a mixture of about 40% dimethylfulvene and 60% isomer mixture (4 and 5) was used as the starting material, changes in composition of the mixture had become slow when 3.5 \pm 1% isomer mixture was left, but the glpc peaks were not clearly resolved as they were when dimethylfulvene was the starting material.

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(17) Perkin-Elmer Model 337 and Cary Model 14 spectrophotometers were used to obtain infrared and ultraviolet spectra, respectively. Mass spectra were determined with an AEI MS-9 instrument and pmr spectra with Varian A-60 and A-100 spectrometers.

(18) W. Freiesleben, *Angew. Chem.*, **75**, 576 (1963).